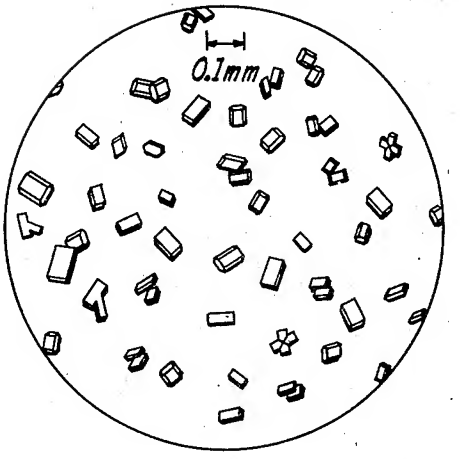
Sept. 24, 1946. F. M. GARFIELD ET AL 2,408,059

MANUFACTURE OF DIAZODINITROPHENOL

Filed July 3, 1940

Fig. 1



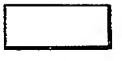


Fig. 2

Fig. 3

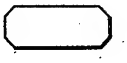


Fig. 4

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MANUFACTURE OF DIAZODINITROPHENOL

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10 Claims. (Cl. 260—141)

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This invention relates to explosives, and more particularly to diazodinitrophenol of novel form and a methol for making the same.

Diazodinitrophenol, first prepared and described by Griess in Annalen, vol. 106, page 123, (1858), has received extensive use in recent years as an ingredient of blasting detonators and ammunition priming compositions. For such use, it is frequently of advantage to utilize a free-flowing form of the explosive. Such a form, consisting of a dark brown, granular powder, was described in Industrial and Engineering Chemistry, vol. 25, page 664, (1933). Also, the preparation of rounded sandy grains of diazodinitrophenol has been described as resulting from the addition of an acid to a suspension of sodium picramate in a sodium nitrite solution in the presence of an added substance adapted to cause this form of precipitate. However, the free-flowing varieties of diazodinitrophenol heretofore described have consisted of opaque agglomerates of large numbers of small needle-like crystals and/or extremely minute particles.

An object of the present invention is to provide an improved form of diazodinitrophenol consisting of free-flowing crystals.

A further object of the invention is to provide a simple process for the precipitation of diazodinitrophenol wherein crystals are obtained which settle rapidly from suspension in a liquid and which flow freely in the dry state.

Another object of this invention is to provide a process for the precipitation of diazodinitrophenol wherein desirable crystals of the explosive are produced through the agency of a crystal growth control ingredient.

In accordance with this invention, the precipitation of diazodinitrophenol is carried out by adding a salt of nitrous acid to a solution or suspension of picramic acid, containing an added acid and a small amount of an ingredient having the property of being adsorbed on the crystals as they form in the reaction mixture and thereby of exerting a desirable control on the crystal growth. The resulting diazodinitrophenol precipitate consists of individual crystals having such dimensions as to promote rapid settling from suspension and to impart the property of free flow in the dry state. The action of the crystallization controlling ingredient is such as to prevent growth of the crystals into the elongated columnar or acicular type heretofore known and

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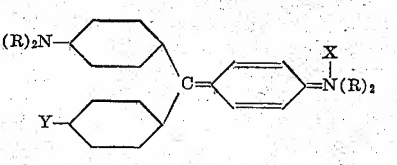
to promote the formation of crystals having dimensions of length and width of the same order of magnitude.

Accordingly, the process of this invention permits the obtainment of a desirable form of precipitated diazodinitrophenol in the form of individual crystals, as distinguished from the agglomerated free-flowing varieties of the explosive which have heretofore been described. The present crystalline form is further distinguished by clarity, an excellent degree of purity and stability, and resistance to disintegration into fine particles.

Precipitation of the diazodinitrophenol in accordance with this invention may be carried out by preparing an aqueous suspension of picramic acid, as by mixing a picramate such as that of sodium, potassium, ammonium, or magnesium, with an excess of a suitable acid such as hydrochloric, sulfuric, or phosphoric, then adding an ingredient, such as is hereinafter specified, which is adapted to control the growth of crystals as desired, cooling the mixture to a suitable reaction temperature, and then gradually adding a solution of nitrite, such as sodium or potassium nitrite.

Triphenylmethane dyes having the following structure have been found useful as crystal growth control ingredients:



In this structural diagram, R is an alkyl group, for example methyl, ethyl, propyl or butyl; X is a halogen atom; and Y is a substituted ammonium or amine group. In the following dyes which have been found particularly suitable, R consists of the methyl group, X is chlorine, and Y is as follows:

	Y
Methyl green	$N(CH_3)_3Cl$.
Ethyl green	$N(CH_3)_2(C_2H_5)Br$.
Methyl violet 3 B	$NHCH_3$
Crystal violet	$N(CH_3)_2$.
Heptamethyl p - rosaniline chloride p-toluenesulfonate	$N(CH_3)_3.OSO_2.C_6H_4CH_3$

Methyl and ethyl green, representative of heptaalkyl p-rosaniline halides are especially advantageous for use in accordance with this invention, for example in the form of their zinc chloride or similar salt addition compounds.

These crystal growth control ingredients are effective for the intended purpose when used in small proportions, for example about 0.5% to 2.0% of the weight of picramate employed. The compounds need not be in a pure state, and may therefore be employed as commercially available, generally having a content of inert material. Furthermore, a mixture of two or more of the substances may at times be used to advantage. When a change in the crystal growth control ingredient is contemplated, any modification in the proportion which is made necessary by the change can readily be established by the results of small scale experiments testing the effect of varied amounts.

The dyes listed above are all characterized as displaying a green coloration in acid solution; other triphenylmethane dyes having this property have also been found suitable for use. For example, the application of the reaction product of malachite green and methyl p-toluene sulfonate, pentamethyl-diaminotriphenyl chloride p-toluenesulfonate, in the present procedure results in desirable free-flowing crystals of diazodinitrophenol.

It is essential for securing the desired results that the precipitation of the diazodinitrophenol be effected by adding the sodium (or other) nitrite to a mixture of the other reagents (picramic and added acid), the crystal growth control agent being contained either in the latter mixture or partly in the mixture and the remainder in the nitrite solution. Reversal of the precipitation procedure, that is the gradual addition of acid to a mixture of the picramate, nitrite, and dye, results in the precipitation of elongated needle crystals rather than the desirable crystals of this invention.

In order to illustrate the invention, procedural details are given in the following specific examples:

Example I

6.0 g. of methyl green, No. 684 in the Colour Index published by the Society of Dyers and Colourists and edited by Dr. F. M. Rowe, 1st ed. 1924, (biological stain grade containing about 59% of the anhydrous zinc chloride double salt of heptamethyl-p-rosaniline chloride) were added to a suspension of 480 g. of pure sodium picramate in 6000 cc. water. The resulting suspension was acidified with a solution of 386 cc. of hydrochloric acid (containing 415.8 g. of HCl per liter) diluted with 480 cc. water, and the mixture was cooled to 11° C. by means of a suitable cooling bath. A solution of 163 g. of sodium nitrite in 720 cc. water was then added uniformly over a period of 25 minutes during continued agitation, the temperature of the reaction mixture being maintained at 11°±1° C. The mixture was then agitated for an additional hour at this same temperature. Agitation was then stopped, the precipitate allowed to settle, and the supernatant mother liquor decanted. The crystalline precipitate was washed three times by suspension with distilled water at a temperature of 5° C., the precipitate being allowed to settle and the wash water removed by decantation in each instance. The product was then stored in the moist state for several hours, when a final cold water wash was applied. The diazodinitrophenol crystals were obtained in a yield of about 400 g. (dry basis), in the form of a paste containing 60%–65% solids.

Example II

To 5500–6500 cc. of water in a suitable container there were added during agitation 480 g. of pure sodium picramate, then 5.2 g. of ethyl green, Color Index No. 685, biological stain grade containing about 76% of the anhydrous zinc chloride double salt of ethyl hexamethyl p-rosaniline chlorobromide, and about 410 cc. of hydrochloric acid (containing 415.8 g. of HCl per liter) diluted with 480 cc. of water. The mixture was cooled to a temperature of about 10° C. by means of a suitable cooling bath. During continued agitation, 780 cc. of a solution containing 150 g. of sodium nitrite were added at a uniform rate such that the addition was completed in 25 minutes, the temperature being maintained at 8°–12° C. The reaction mixture was then agitated for another hour at the same temperature. Agitation was then discontinued, the precipitate allowed to settle, and the supernatant mother liquor decanted. The crystalline diazodinitrophenol was then washed and allowed to settle to a paste containing 60%–65% solids, an 85%–90% yield of product being obtained.

The paste of diazodinitrophenol, obtained as described in the above examples, is of desirable consistency for direct use in wet-mixed explosive compositions, and may therefore be stored at constant temperature, in the moist state, until needed. In applications requiring dry explosive, as in the loading of detonators, the diazodinitrophenol produced in accordance with this invention may be dried by any suitable means and yields a product having desirable free-flowing properties.

The diazodinitrophenol produced in accordance with the above examples consists of clear green tabular crystals having, on the average, dimensions of about 0.060 mm. by 0.033 mm. by 0.013 mm. Figure 1 of the accompanying drawing forming part of this specification shows such crystals as they appear by transmitted light under the microscope. The principal crystal faces appear to be substantially rectangular and the crystal edges are frequently bevelled so that the cross section perpendicular to the long axis is rectangular, hexagonal, or octagonal in outline, as shown in Figures 2, 3, and 4 respectively. Twinned crystals may be observed occasionally, and the crystal faces and edges may acquire a pitted or etched appearance as a result of extensive washing. The color imparted by the adsorbed dye permits the identification of the crystals.

These crystals settle rapidly from suspension in liquids to a paste containing 60%–65% solids, flow freely when dry, and, on being poured into a container in this state, have an apparent density of about 0.55 g. per cc.; in contrast, the elongated crystals resulting when a crystal growth control ingredient is not employed during the precipitation, settle slowly from suspension in a liquid to a paste containing 45%–50% solids, tend to form matted lumps when dry, and in this state have an apparent density of about 0.32 g. per cc.

With regard to stability, these crystals appear to be superior to the prior free-flowing forms of diazodinitrophenol, as illustrated by the com-

parative results of hot moist storage tests shown in the following table:

	Rounded sandy grains	Prior elongated crystals	Crystals of this invention
Original weight.....grams..	1.000	1.000	1.000
Original instantaneous flash point.....° C..	210	210	210
After 26 days' storage at 74° C. and 85 per cent relative humidity; weight.....grams..	0.835	0.908	0.900
Instantaneous flash point..° C..	[1] 260	210	210

[1] Weak explosion.

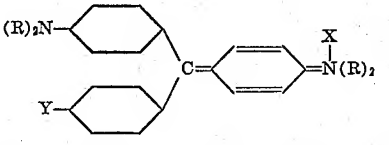
Accordingly, the purity and stability of the novel crystalline diazodinitrophenol render it outstanding for use in detonators and in ammunition priming compositions.

It is to be understood that the procedural details given above are purely illustrative and that a desirable product may be obtained in modifications of the described procedure within the spirit of the invention, which accordingly is not to be limited to such details.

Having now described the invention, what is claimed as new and is desired to be secured by Letters Patent, is:

1. As a new product, free-flowing diazodinitrophenol in the form of tabular crystals containing an adsorbed triphenylmethane dye.

2. As a new product, free-flowing diazodinitrophenol in the form of tabular crystals containing an adsorbed dye having the following structure:



where R is an alkyl group, X is a halogen, and Y is a member of the group consisting of substituted ammonium and amine groups.

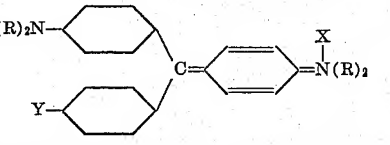
3. As a new product, free-flowing diazodinitrophenol in the form of tabular crystals containing a hepta-alkyl p-rosaniline halide.

4. As a new product, free-flowing diazodinitrophenol in the form of tabular crystals containing ethyl hexamethyl p-rosaniline chlorobromide.

5. As a new product, free-flowing diazodinitrophenol in the form of tabular crystals containing heptamethyl p-rosaniline chloride.

6. In the manufacture of diazodinitrophenol, the process comprising gradually adding a nitrite to a mixture of picramic acid and an added acid in the presence of a triphenylmethane dye.

7. In the manufacture of diazodinitrophenol, the process comprising gradually adding a nitrite to a mixture of picramic acid and an added acid in the presence of a triphenylmethane dye having the following structure:



where R is an alkyl group, X is a halogen, and Y is a member of the group consisting of substituted ammonium and amine groups.

8. In the manufacture of diazodinitrophenol, the process comprising gradually adding a nitrite to a mixture of picramic acid and an added acid, in the presence of a heptaalkyl p-rosaniline halide.

9. In the manufacture of diazodinitrophenol, the process comprising gradually adding a nitrite to a mixture of picramic acid and an added acid, in the presence of ethyl hexamethyl p-rosaniline chlorobromide.

10. In the manufacture of diazodinitrophenol, the process comprising gradually adding a nitrite to a mixture of picramic acid and an added acid, in the presence of heptamethyl p-rosaniline chloride.

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